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Enhancement of molecular polarizabilities by the push-pull mechanism; a DFT study of substituted benzene, furan, thiophene and related molecules

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Abstract: We report Density Functional Theory (DFT) studies of the dipole polarizabilities of benzene, furan and thiophene together with a number of substituted and related systems. All geometries were optimized (and characterized) at the B3LYP/6-311g(2d,1p) level of theory and polarizabilities then calculated with B3LYP/6-311++G(2d,1p). For the R-ring systems we find group polarizabilities in the order R = $NO_2 \sim OCH_3 \sim CN \sim CHO > NH_2 > OH > H = 0$. For systems R-ring-R, $<\alpha>$ differs little from the additivity model, with small positive and negative increments. For systems D-ring-A (where D and A are deactivating and activating groups) we find a positive enhancement to $<\alpha>$ over and above the value expected on the basis of pure additivity for all pairs A and D studied. This enhancement can be increased greatly by extending the length of the conjugated chain to D-ring-CH=CH-ring-A and D-ring-N=N-ring-A systems. Empirical models of polarizability such as AM1 agree badly with the DFT calculations in an absolute sense but give excellent statistical correlation coefficients. Calculated $<\alpha>$'s also agree well in a statistical sense with the molecular volumes calculated from molecular mechanics force fields

Analysis of the results in terms of the π electrons alone is not satisfactory.

Keywords: Density functional theory (DFT), molecular dipole, dipole polarizability, QSAR, group polarizability, group additivity, benzene, furan, thiophene. Susbtituents. Push-pull mechanism

1 Introduction

The electric dipole moment $\mathbf{p}_e$ of a molecule is a quantity of fundamental importance in structural chemistry. When a molecule is subject to an external electric field $\mathbf{E}$, the molecular charge density may rearrange and hence the dipole moment may change [1]. This change can be described by the equation

$$\mathbf{p}_e = \mathbf{p}_0 + \alpha : \mathbf{E} + \frac{1}{2}\beta : \mathbf{EE} + ... \tag{1}$$

Here α is a second rank tensor property called the dipole polarizability, β is the first of an infinite series of dipole hyperpolarizabilities and $\mathbf{p}_0$ the permanent electric dipole moment. If the electric dipole moment does indeed change when an external field is applied, the molecular potential energy U will also change according to equation (2)

$$U = U_0 - \mathbf{p}_e.\mathbf{E} - \frac{1}{2}\alpha : \mathbf{EE} - \frac{1}{6}\beta : \mathbf{EEE} - \tag{2}$$

Hyperpolarizabilities are generally small in magnitude, and their effect is minimal for weak electric fields. Molecules that exhibit large α and β values are of current interest because of their applications to electro optical devices [2, 3] and in the general field of non-linear optics (NLO). One general aim in this relatively new field of endeavour is to design molecules having specific values of α and β.

In this paper we concern ourselves with α and in particular the mean value $<\alpha>$ defined in terms of (for example) the principal axes a, b and c as

$$\langle\alpha\rangle = \frac{1}{3}\left(\alpha_{aa} + \alpha_{bb} + \alpha_{cc}\right) \tag{3}$$

Many of the aims and objectives of molecular electronics are similar to those of traditional dyestuff chemistry and there is much that is relevant from studies in this older field [4]. If a molecule contains two unsaturated groups that are far apart and separated by a chain of saturated atoms, then the absorption spectrum of the molecule is essentially that of an equimolar mixture of the two component groups in isolation [5]. It is only when the two groups are joined together by a conjugated chain that the spectrum shows large deviations from this additivity rule. Linear conjugated chains of carbon atoms are important chromophores in naturally occurring pigments such as the carotenes and in artificial pigments such as cyanine dyes. Chains that include benzene rings joined by –N=N- groups form the basis for azo dyes. Many such relevant molecules can be represented by the idealized structure shown in Figure 1.

It is widely believed that both dyestuff and NLO materials can be designed to order by modifying the activating group A, the size and complexity of the conjugated system, and the deactivating group D. It is also thought that the presence of an activating group together with a deactivating group in suitable ring positions can enhance some electronic properties. The well-known phrase 'push-pull mechanism' is used to describe such behaviour.

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Fig. 1 Schematic NLO/ dyestuff molecule. A = activating group, D = deactivating group.

Push-pull mechanisms are widely cited in the chemical and biological literature. For example, in a long series of papers ten Brink et. al [6] have discussed various aspects of catalytic conversions in water. In Part 22 they report on electronic effects in the (ligand)Pd^{II} – catalysed aerobic oxidation of alcohols, and give data for a range of catalyst and benzyl alcohols. They conclude that a push-pull mechanism is operative since the presence of both activating groups on the benzyl alcohol and deactivating groups on the 4,4'-disubstituted-2-2'bipyridine ligand increase the reaction rate. As a second example, Banin et. al. [7] report an investigation into injuries caused by the chemical warfare agent mustard gas. They conclude that either zinc- or gallium-desferrioxamine, by virtue of their ability to infiltrate cells and inhibit (by a push-pull mechanism) the transition metal-dependent formation of free radicals, can be used as a basis for treatment for mustard injuries.

In an interesting example of role reversal, Lee, Kim and Mhin [8] report a simple expression of the amount of intramolecular charge transfer of π-electron push-pull systems based on the electronegativity and polarizability of the corresponding push and pull components. Their interesting calculations were done at the B3LYP/6-31+G* level of theory.

The phrase is also used in other branches of human endeavour. For example, Bartels and Zeki [9] report a neuroscientific study of romantic and maternal love. They conclude that "human attachment employs a push-pull mechanism that overcomes social distance by deactivating [neural] networks used for critical social assessment and negative emotions, whilst it bonds individuals through the involvement of the reward circuitry, explaining the power of love to motivate and exhilarate".

We should also mention that the descriptors '(electron) donor' and '(electron) acceptor' were widely used for many years rather than 'activating' and 'deactivating'.

Returning to the topic of dipole (hyper)polarizability, a number of systems typified by Figure 1 have been studied in recent years. Albert, Morley and Pugh [10] gave an AM1 study of various donor-acceptor phenylazobenzenes, phenylazonaphthalenes, phenylazoanthracenes and phenylazoheterocyclics. One conclusion was that the replacement of a phenyl ring by naphthalene or anthracene led to a modest increase in the polarizability and dipole hyperpolarizability.

In their definitive work, Jug, Chiodo and Janetzko [11] reported density functional theory (DFT) calculations of the dipole moments, polarizabilities and first hyperpolarizabilities of stilbene analogues. They reported the importance of the length of the π-

electron system and cited the push-pull mechanism. In addition, they made a careful study of solvent effects, which are found to be non-negligible.

The most relevant work is perhaps that of Varanasi et. al [12], who were concerned with the role of heteroaromatics in the design of NLO materials. These authors used AM1 to calculate β for a large number of push-pull substituted conjugated systems with heteroaromatic spacers. They claim that the differences in ground and first excited state dipole moments and transition energies primarily determine the changes in β.

Thus, it is expected that the push-pull mechanism will tend to increase α (and β etc) in a molecule typified by Figure 1 over and above what one would expect from superposition of the isolated constituents.

Finally, we should draw attention to a recent paper [13] where we reported a theoretical study of polarizabilities for the three benzene-ring molecules shown in Figure 2. Here, A and D are a selection of activating and deactivating groups such as NH_2 and NO_2. We found that the presence of an A and a D group does indeed give an enhancement to $<\alpha>$ over and above what would be expected on the basis of the pure additivity of contributions from A and D, and that a (much larger) enhancement could be produced by increasing the complexity/ length of the conjugated system. For the sake of completeness, we will reproduce key results from the short communication [13] in this paper.

The aim of our present paper is to draw together results for three related series of molecules shown in Figure 2, where we replace the benzene ring with furan and thiophene as appropriate.

2 Routes to polarizabilities

We start with a few relevant words of background, in order to clarify the discussion. The experimental determination of a molecular polarizability is far from straightforward, especially if the molecule has little or no symmetry. The principal routes are studies of refractive index and relative permittivities, Rayleigh and Raman scattering and through the quadratic Stark effect. In the gas phase, the mean value $<\alpha>$ can be determined from the refractive index n according to the equation

$$n = 1 + \frac{\langle\alpha\rangle\, p}{2\varepsilon_0 k_B T} \tag{4}$$

where p is the pressure, k_B the Boltzmann constant, T the thermodynamic temperature and ε_0 the permittivity of free space [1].

In a condensed phase, the problem is complicated because the separation between molecules is of the order of molecular dimensions and their interactions can no longer be ignored. As a result both the external field and the field due to the surrounding molecules polarize each molecule. This behaviour can be described by the Clausius-Mossotti equation:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N\,\langle\alpha\rangle}{3\varepsilon_0 V}. \tag{5}$$

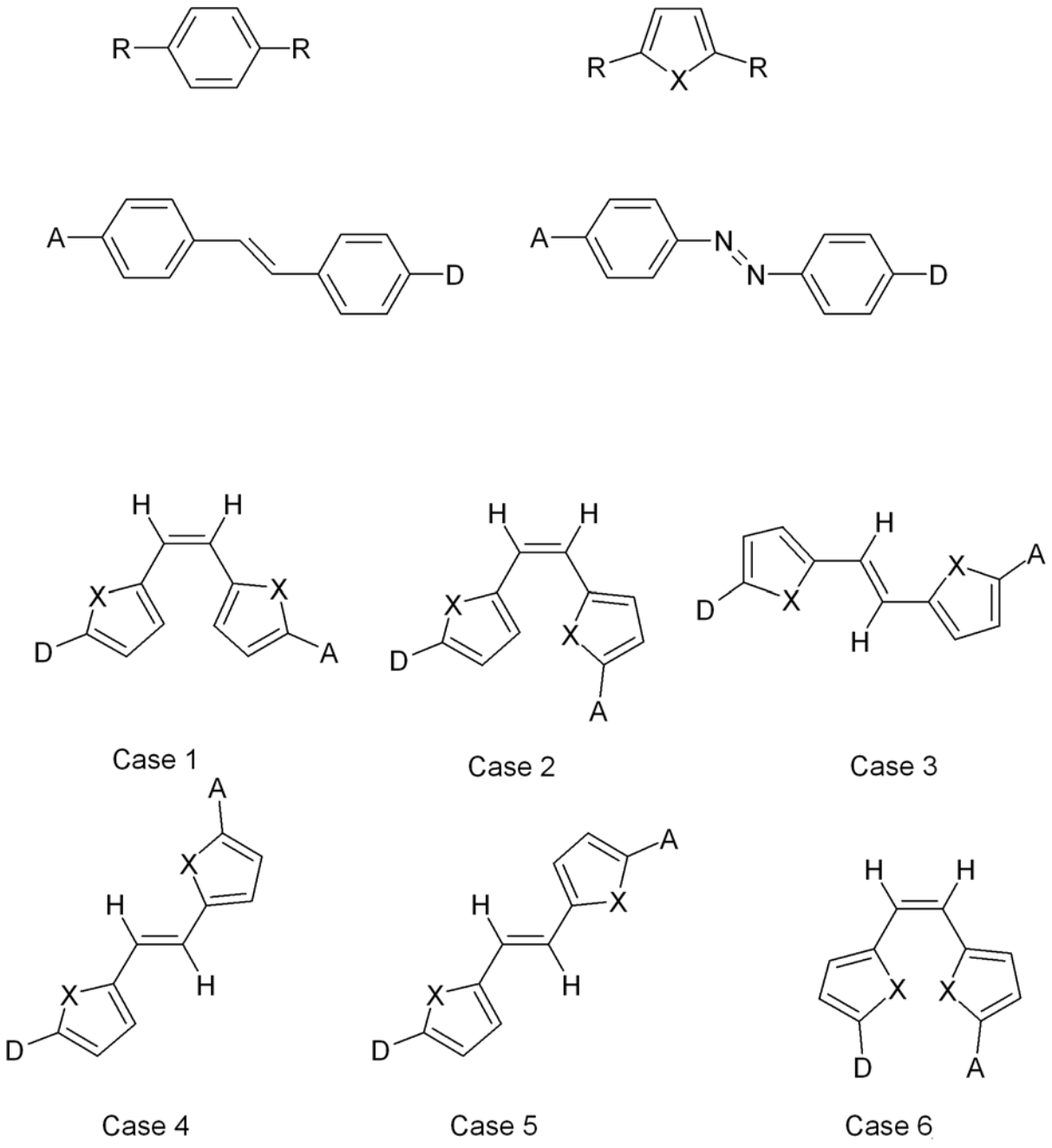


Fig. 2 Structures studied; X = O or S, A = activating group, D = deactivating group, R = generic symbol for group.

Here, N is the number of molecules in volume V. At optical frequencies and in non-magnetic materials eq (5) becomes the familiar Lorenz-Lorentz equation

$$\frac{n^2-1}{n^2+2} = \frac{N\langle\alpha\rangle}{3\varepsilon_0 V} \tag{6}$$

As mentioned above, Jug et. al. [11] reported a rare theoretical study of solvent effects for molecules relevant to the present study.

The quantity of interest is therefore $<\alpha>$. The components of α can sometimes be determined spectroscopically but experimental data is sparse.

An alternative route to polarizability is direct calculation, and there is a large literature [14, 15]. The general idea is to find a level of theory that gives highly accurate values for the polarizability tensor, but naturally this aim has to be moderated with the cost of such calculations. For comparison with the early paper [13], we standardized on the following procedure. Geometries were optimized and characterized at the B3LYP/6-311G(2d,1p) level of theory and B3LYP/6-311++G(2d,1p) polarizabilities were calculated at this geometry. We did not attempt to evaluate the vibrational contribution to these quantities [15]. Likewise we made no attempt to quantify solvent effects [14, 15], and so our calculations refer to gas phase molecules at 0 K. All calculations were done using Gaussian 03W [16], with standard basis sets, integration points, cutoffs etc.

3 Calculations

3.1 Monosubstituted benzenes, furans and thiophenes

First we consider the monosubstituted rings. In the case of furan and thiophene, we only treated substitution at the 1-position.

Rather than discuss the absolute $<\alpha>$ values (which are given in Appendix, Table 1), we concentrate on the values of $<\alpha>$ relative to the unsubstituted ring, as shown in Figure 3. This gives a group increment for each R group in the substituted rings. So for example, $<\alpha>$ is 67.31, 85.68 and 79.43 au for benzene, nitrobenzene and aniline which gives group contributions of 18.37 au for the NO_2 group and 12.12 au for NH_2. All benzene results are taken from Reference [9].

The first point to notice is that our calculated group polarizabilities are roughly constant across the three conjugated ring systems. The chemically-appealing idea that a molecular property such as $<\alpha>$ can be constructed from tables of group contributions is an old one, and if we rewrite the Lorenz-Lorentz equation in molar terms we have

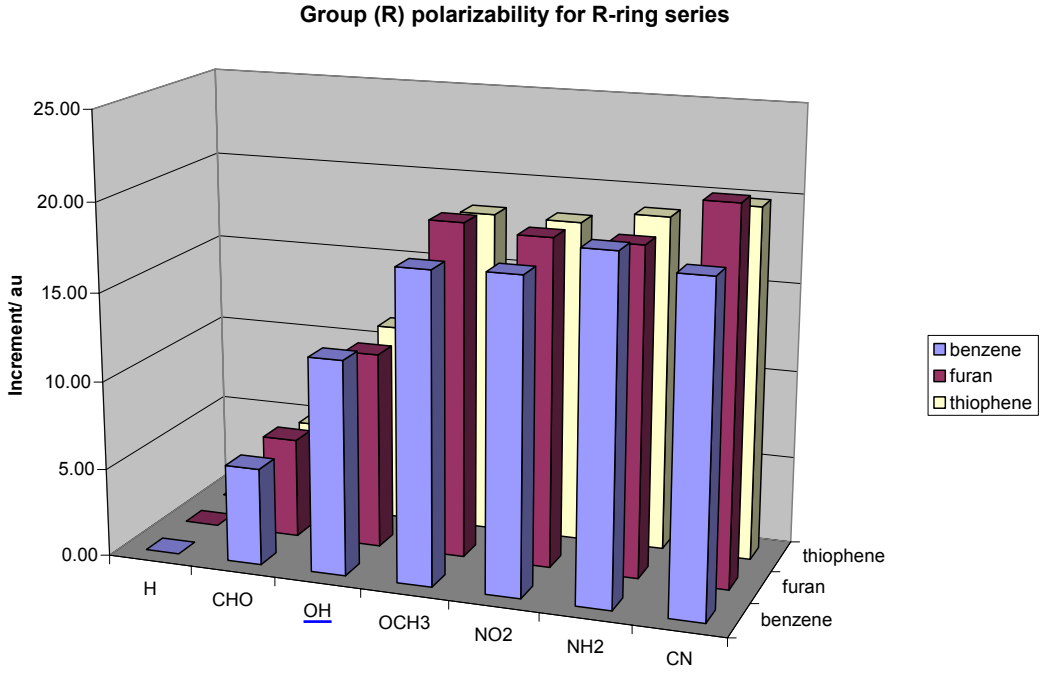
$$\frac{M}{\rho}\frac{n^2-1}{n^2+2} = \frac{N_A \langle\alpha\rangle}{3\varepsilon_0} \tag{7}$$

which defines the *molar refractivity* R_m. The incremental behaviour of R_m was noted many years ago [18, 19] and extensive tables of additive atom and group refractions are available [20]. It is thought to be a reasonable model for rationalizing and predicting R_M across related groups of molecules, but not adequate for disparate groups of molecules. We return to this point later.

The second point of note is that our calculated group polarizabilities are in the order

$$NO_2 \sim OCH_3 \sim CN \sim CHO > NH_2 > \underline{OH} > H(=0)$$

According to a recent textbook in undergraduate organic chemistry [21] the 'organic chemistry' order of our chosen groups from highest activating to highest deactivating is as follows



* We follow convention and record many quantities in atomic units (au). The au of dipole polarizability is $e^2a_0^2E_h^{-1}$ so that 1 au of dipole polarizability = 1.6488×10^{-41} $C^2m^2J^{-1}$.

Fig. 3 Group polarizability = increment between $<\alpha>^*$ for R-ring and ring.

$$NH_2 > OH > OCH_3 > H\ (=0) > -CHO > CN > NO_2$$

with the point on the scale where groups are neither activating or deactivating (H) denoted 'zero'. There is no particular reason why our polarizability increments should agree with Loudon's organic scheme; the latter is to do with the chemical reactivity of a given substituted molecule C_6H_5X compared to benzene, ours to do with the response of the ground state molecule C_6H_5X to an applied electric field. Our group polarizability scheme is the one to be used for polarizability calculations.

3.2 Disubstituted benzenes, furans and thiophenes

The next step is to investigate the value of $<\alpha>$ for the disubstituted single ring compounds illustrated in Figure 2. We consider first the case where A = D (denoted R for simplicity) and these results are given in Appendix, Table 2. In view of the discussion above, it is interesting to investigate the deviations from group additivity, so for example consider benzene ($<\alpha>$ = 67.31 au) and 1,4-dinitrobenzene ($<\alpha>$ = 104.60 au). We would expect $<\alpha>$ for dinitrobenzene to be 67.31 + 18.37 + 18.37 au = 104.11 au on the basis of group additivity. The calculated value of 104.60 gives a deviation from additivity of +0.49 au. The full results are illustrated in Figure 4.

The calculated deviations from group additivity when the two susbtituents are the same are generally small in magnitude and either positive or negative with no obvious trend. They are however consistent across the different ring systems.

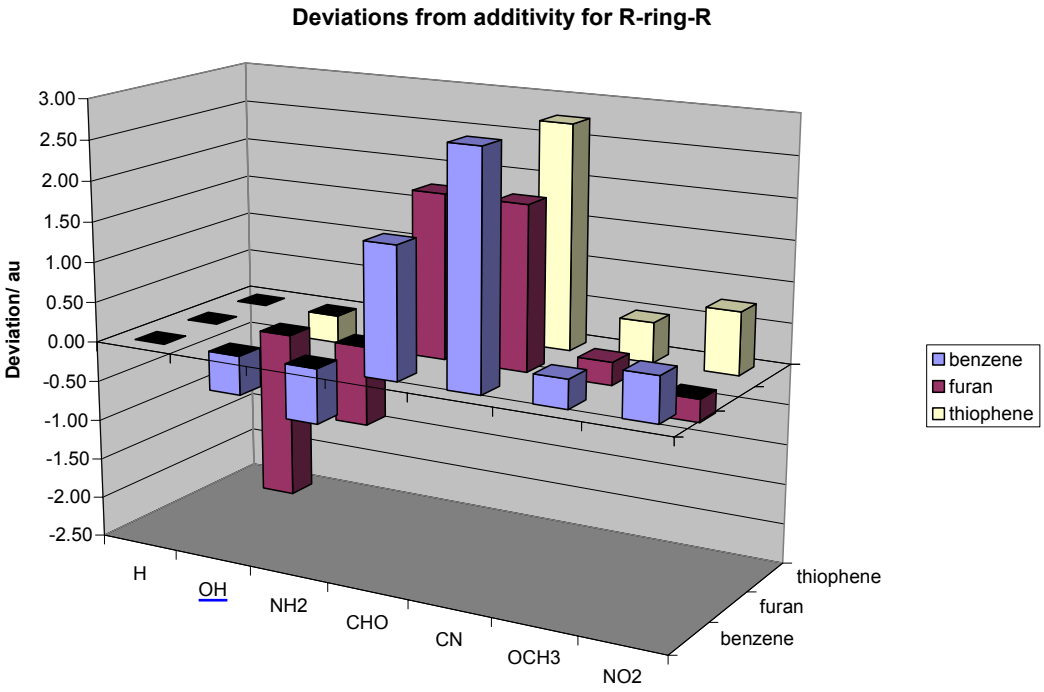


Fig. 4 Deviations from additivity for R-ring-R.

We now turn to the case of D-ring-A with the following selection of D,A groups; OH, CN; NH_2,CN; OH, CHO; NH_2, CHO; OCH_3, NO_2; OCH_3, CN; OCH_3, CHO; NH_2, NO_2; OH, NO_2. The numerical results are given in Appendix Table 3, and the deviations from additivity are illustrated in Figure 5.

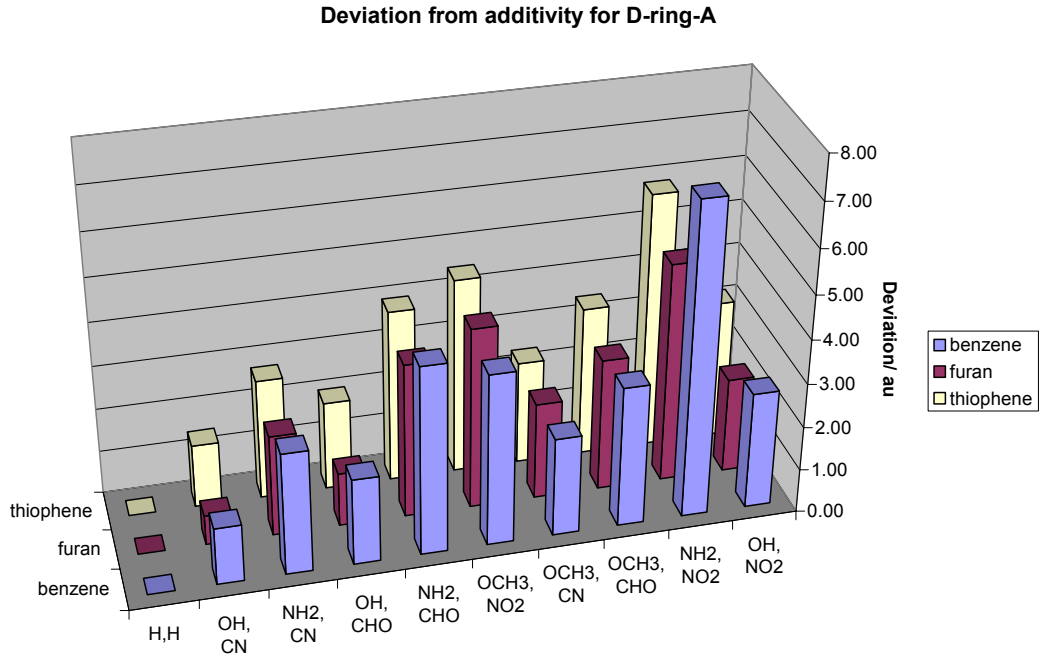


Fig. 5 Deviations from additivity for D-ring-A.

In all cases there is an enhancement to $<\alpha>$ over and above what one would expect from the simple additivity model. This is evidence of the push-pull mechanism, and the largest enhancement is for the NH_2, NO_2 pair in the case of all three rings studied, which interestingly corresponds to the two groups at the extremes of Loudon's organic chemistry scheme. The OH, CN and the OH, CHO pairs give the poorest enhancement, with the remaining pairs occupying the middle ground.

3.3 Extended conjugated systems

Having investigated the behaviour of $<\alpha>$ for D-ring-A, we turn attention to the extended conjugated systems illustrated in Figure 2. There are six possible geometric conformations for the furan and thiophene –CH=CH- and –N=N- chains and the total energies are shown in Appendix Table 4.

All extended ring polarizability calculations were done with geometry 3 and susbtituents at the 1 ring position illustrated. Figure 6 shows the deviations from additivity for the cases D-ring-CH=CH-ring-A.

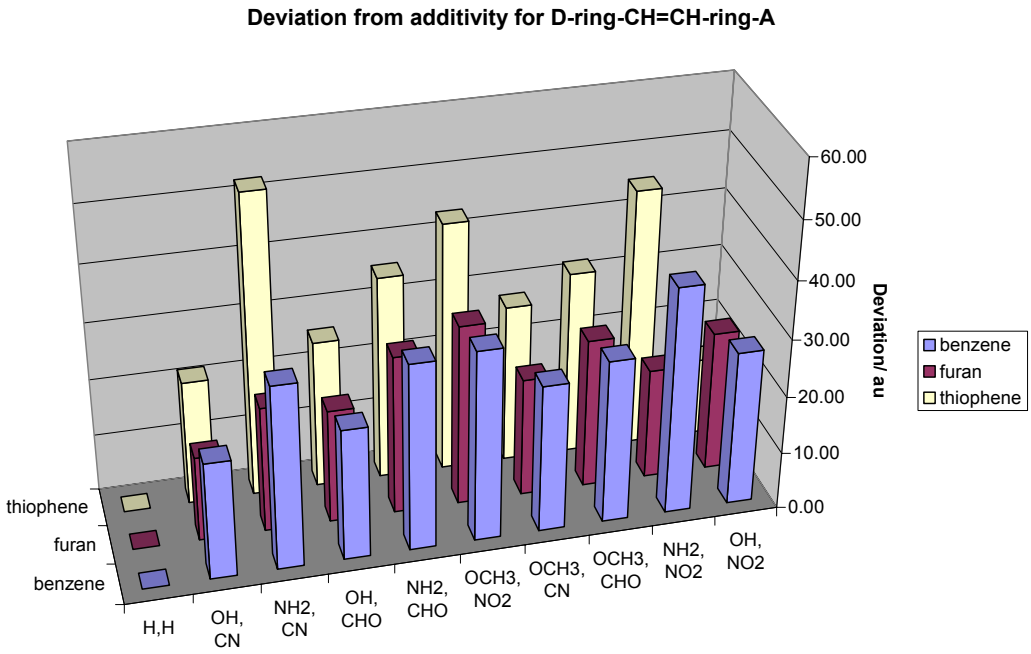


Fig. 6 Deviation from additivity.

In all cases, the deviation from the group additivity model is large and positive. The poorest pairings are generally OH, CN and OH, CHO.

Figure 7 shows corresponding results for the cases D-ring-N=N-ring-A.

Once again deviations from the group additivity model are all large and positive.

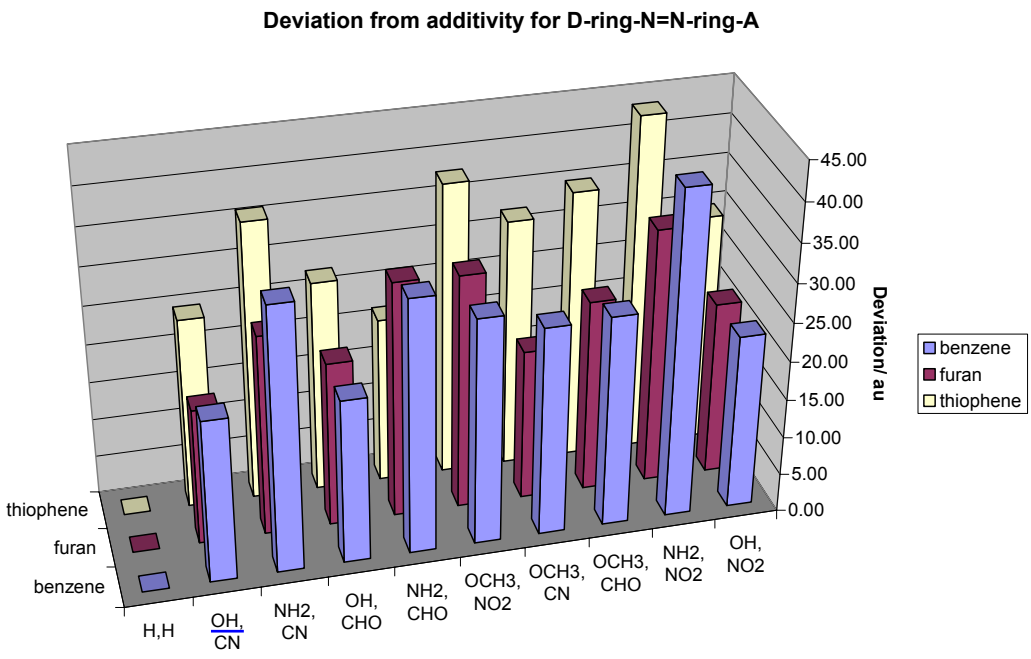


Fig. 7 Deviations from additivity.

4 Discussion and analysis

4.1 Molecular volumes and semiempirical calculations

Dipole polarizabilities are often used in QSAR studies, where the aim is to give a reliable but quick estimate of $<\alpha>$ along with the molecular surface area, the volume and log(K) as part of the process of high-throughput screening. *Ab Initio/* DFT polarizability calculations are prohibitively expensive in a QSAR context, even for such simple molecules. One therefore looks to less rigorous but reliable procedures.

Consider therefore a typical neutral atom modelled as the sphere of charge shown in Figure 8 The radius is a and the nuclear charge is Q. We switch on the electric field E which displaces the nucleus by a relative distance d from the original atomic centre.

At this point there is a force on the nucleus QE due to the applied field and one due to the electron density. According to Gauss' electrostatic theorem [1], the latter force is

$$\frac{Q^2 d}{4\pi\varepsilon_0 a^3} \tag{8}$$

At equilibrium these two forces must be equal and so the displacement d satisfies

$$\frac{Q^2 d}{4\pi\varepsilon_0 a^3} = QE \tag{9}$$

The induced electric dipole moment is Qd and the polarizability is Qd / E hence

$$\alpha = 4\pi\varepsilon_0 a^3 \tag{10}$$

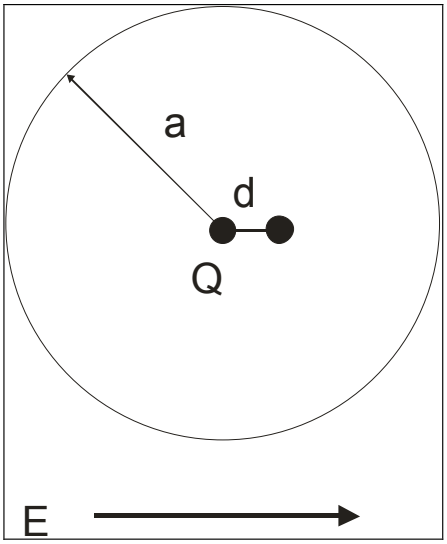


Fig. 8 Atom in external electric field.

The derivation can be easily extended to a closed volume of arbitrary shape, not necessarily a sphere, and apart from the factor $4\pi\varepsilon_0$ the polarizability of a molecule is determined in this model by its volume. For this reason, workers in the field speak about 'polarizability volumes' and quote their results in volume units.

Molecular volumes are routinely determined in QSAR studies, and typical values calculated using molecular mechanics are shown in Table 7 for the series D-furan-CH=CH-furan-A. The numerical conversion factor between $\mathrm{\AA}^3$ and atomic units of polarizability is

$$\frac{4\pi\varepsilon_0 \times 10^{-30}}{1.6488 \times 10^{-41}} = 6.748$$

and so the prediction from this simple model would be $<\alpha> = 6.748 \times 529$ au $= 3570$ au for the first compound (D = A = H), compared to the DFT value of 155.0 au. Whilst the quantitative agreement with experiment is clearly nonexistent, our molecular volumes do give a good least square fit to the DFT mean polarizability values. For example, correlating DFT $<\alpha>$'s against molecular volumes for all the furan molecules studied gives a linear correlation coefficient of 0.95.

The additivity hypothesis has been repeatedly criticized [22] on the grounds that it neglects the interactions between the various groups in a molecule. The definitive reference in this field appears to be that due to K J Miller [23]. Miller pointed out the need to take account of the atomic environment in molecular calculations, and this is usually done by assigning parameters in which each atom is characterized by its state of atomic hybridization. Miller and Savchik [24] proposed a functional form

$$< \alpha >= 4\pi\varepsilon_0 \frac{4}{N} \left(\sum_A^{\tau_A} \right)^2 \tag{11}$$

where τ_A is an atomic hybrid component for each atom A in a given state of hybridization. N is the total number of electrons. In fact, Miller and Savchik omitted the factor $4\pi\varepsilon_0$ and

so most computer packages quote the results as polarizability volumes (typically Å^3). The Miller method gives much more reasonable $<\alpha>$'s as illustrated in Table 7. It is clear that the Miller-Savchik polarizability volumes are not to be interpreted as molecular volumes. A linear regression between the Miller-Savchik and our DFT $<\alpha>$ for all furan molecules included in the study gives a regression coefficient of 0.96.

5 The π-electrons

In the early days of modern electronic structure theory (the 1960s and early 1970s) much attention focused on the structure and electronic properties of π-electron molecules. This was because such molecules are intrinsically very interesting, but also because early computers could only handle (for example) Pariser-Parr-Pople π-electron models for large molecules. Polarizability calculations were rare, and in any case seriously flawed because typical semiempirical models use a minimal basis set, which is certainly inadequate. It seems to be still widely believed [ref 5c and references therein] that the push-pull mechanism is dominated by the π-electrons. In order to investigate this possibility in the present context, we give an analysis of the π-electron polarizability contribution for some of the title molecules.

The π-electron contributions $<\alpha>_\pi$ for the R-ring series are shown in Table 1. The ordering

$$OCH_3 \gg NH_2 \sim CN \sim CHO \sim NO_2 > \underline{OH} > H\ (=0)$$

is at variance with that found for the full $<\alpha>$ in that the OCH_3 group contribution is now dominant. One conceptual difficulty with the π-electron analysis is that (for example) $PhOCH_3$ is not a true π-electron molecule because the CH_3 group hydrogens lie out of the benzene-O plane. Analysis in terms of the π-electrons alone cannot explain the push-pull effect, but the π-electrons do indeed mirror the behaviour of the total electron density in that the D-ring-A molecules show larger enhancements to $<\alpha>_\pi$ than that expected from a comparison with the R-ring-R series.

6 Conclusions

Group polarizability values are in the order

$$NO_2 \sim OCH_3 \sim CN \sim CHO > NH_2 > OH > H$$

Group polarizabilities are (roughly) constant across the three substituted rings R-ring, where ring = benzene, furan and thiophene.

Deviations from group additivity are small and of either magnitude for R-ring-R

Deviations from group additivity are larger and always positive for the series D-ring-A studied. This gives overall support to the well-known 'push-pull' mechanism.

Increasing the complexity/ length of the conjugated system leads to a large increase in this deviation from pure additivity

Empirical models based on molecular volumes give unrealistic values for $<\alpha>$ but these values correlate well with the DFT results.

The Miller-Savchik scheme gives poor absolute $<\alpha>$'s but the results correlate well with those derived from DFT.

Appendix of Tabular Data

All DFT calculations were done using Gaussian/ G03 [16]. Geometries were optimized at the B3LYP/6-311G(2d,p) level of theory and all stationary points characterised by calculation of the Hessian eigenvalues, in the normal manner. Polarizabilities were then calculated at this geometry but at the B3LYP/6-311++G(2d,p) level of theory.

Molecular volumes and empirical polarizabilities were found from optimized MM2 geometries using HyperChem v7 [17]. The Miller-Savchik polarizabilities were also found using this software.

Table 1 $<\alpha>$ for R-ring molecules, together with the π-electron contribution.

	benzene		furan		thiophene	
	$<\alpha>$/ au	$<\alpha>_\pi$/ au	$<\alpha>$/ au	$<\alpha>_\pi$/ au	$<\alpha>$/ au	$<\alpha>_\pi$/ au
R = H	67.31	43.06	47.17	33.63	62.21	42.78
CHO	84.77	47.74	66.10	38.08	80.56	47.06
OH	72.80	44.84	52.82	35.73	67.27	44.64
OCH_3	85.66	57.08	65.66	45.58	81.17	54.84
NO_2	85.68	47.10	68.25	37.67	82.09	46.26
NH_2	79.43	49.15	58.29	40.33	73.56	48.90
CN	84.92	48.19	65.67	38.68	80.49	47.387

Table 2 $<\alpha>$ for R-ring-R molecules, together with the π-electron contribution.

	benzene		furan		thiophene	
	$<\alpha>$/ au	$<\alpha>_\pi$/ au	$<\alpha>$/ au	$<\alpha>_\pi$/ au	$<\alpha>$/ au	$<\alpha>_\pi$/ au
R = H	67.31	43.06	47.17	33.63	62.21	42.78
CHO	103.86	52.81	87.03	44.01	100.16	52.06
OH	77.81	46.20	56.41	37.38	71.97	46.14
OCH_3	106.19	67.39	84.42	60.00	100.62	68.71
NO_2	104.60	51.95	89.06	42.97	102.74	50.90
NH_2	90.87	55.05	68.43	46.20	85.11	55.04
CN	105.40	53.84	86.17	44.41	101.53	52.68

Table 3 $<\alpha>$ for D-Ring-A, together with the π-electron contribution.

	benzene		furan		thiophene	
	$<\alpha>$/ au	$<\alpha>_\pi$/ au	$<\alpha>$/ au	$<\alpha>_\pi$/ au	$<\alpha>$/ au	$<\alpha>_\pi$/ au
D,A = H,H	67.31	43.04	47.17	33/63	62.21	42.78
OH, CN	91.72	49.96	71.99	40.66	86.99	49.23
NH_2, CN	99.82	53.78	79.10	44.74	94.58	53.18
OH, CHO	92.24	49.46	72.97	40.02	87.64	48.75
NH_2, CHO	101.20	53.30	80.75	44.15	95.85	52.70
OCH_3, NO_2	108.86	59.22	90.88	50.07	105.53	58.48
OCH_3, CN	106.44	60.37	86.37	51.16	101.81	59.70
OCH_3, CHO	107.25	59.91	87.61	50.52	102.95	59.43
NH_2, NO_2	104.93	54.76	84.39	43.52	99.30	51.86
OH, NO_2	93.83	48.85	76.07	39.63	90.31	48.09

Table 4 Energies/ E_h* for ring-CH=CH-ring etc.

	furan		thiophene	
	CH	N	CH	N
1	-536.413330	-568.448378	-1182.379008	-1214.414436
2	-536.415903	-568.451829	-1182.379068	-1214.417202
3	-536.422688	-568.474257	-1182.388383	-1214.457702
4	-536.420220	-568.473668	-1182.386716	-1214.444822
5	-536.418193	-568.473467	-1181.905996	-1214.440125
6	-536.413463	-568.452449	-1181.860237	-1214.439765

* The atomic unit of energy, $E_h = 4.3598 \times 10^{-18}$ J (equivalent to 2625.5 kJ mol^{-1})

Table 5 $<\alpha>$ / au for D-Ring-CH=CH-Ring-A.

	benzene	furan	thiophene
H,H	192.13	155.00	186.32
OH, CN	235.59	193.92	231.31
NH_2, CN	253.78	206.51	268.43
OH, CHO	237.95	199.34	235.44
NH_2, CHO	254.24	212.75	251.55
OCH_3, NO_2	262.06	226.07	268.52
OCH_3, CN	253.82	212.62	251.13
OCH_3, CHO	256.42	218.44	255.71
NH_2, NO_2	262.15	206.45	262.62
OH, NO_2	242.92	206.11	224.71

Table 6 <α>/ au for D-Ring-N=N-Ring-A.

	benzene	furan	thiophene
H,H	183.82	156.07	187.22
OH, CN	227.98	197.87	235.34
NH_2, CN	247.79	211.73	252.90
OH, CHO	228.07	202.03	238.02
NH_2, CHO	246.26	216.74	238.44
OCH_3, NO_2	249.86	226.07	263.95
OCH_3, CN	246.88	212.62	256.62
OCH_3, CHO	247.03	218.44	259.47
NH_2, NO_2	256.50	221.42	261.99
OH, NO_2	230.35	205.33	241.90

Table 7 Various quantities for D-furan-CH=CH-furan-A.

	<α> (DFT) / au	Volume/ Å^3	<α> (Miller)/ Å^3
H,H	155.00	529	17.89
OH, CN	193.92	613	20.38
NH_2, CN	206.51	625	21.09
OH, CHO	199.34	612	20.45
NH_2,CHO	212.75	623	21.16
OCH_3, NO_2	226.07	679	22.20
OCH_3, CN	192.62	671	22.21
OCH_3, CHO	218.44	670	22.28
NH_2, NO_2	206.45	632	21.08
OH, NO_2	206.11	622	20.37

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